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16. ABSTRACT

Nine natural waters were evaluated to define the effects of temperature, pH, chlorine dose, bromide ion concentration, precursor source and concentration, and reaction time on the formation of THM-Br and the related conversion of inorganic bromide to THM-Br.

In THM formation a portion of the inorganic bromide ion concentration is converted to organically bound bromine in the three common brominated THM species. This percentage conversion (1) increases rapidly in the first stages of THM formation and approaches a plateau at longer reaction times; (2) increases with increasing pH and increasing temperature; (3) increases with chlorine concentration but approaches a plateau at high concentrations; (4) initially increases with Br^- concentration to a maximum percentage conversion and subsequently decreases at higher Br^- concentrations.

It was difficult to define clear trends for the variation of percentage conversion with THM precursor source and concentration presumably because of multiplicative effects of variables as well as parameters such as ammonia concentration that were not examined in this study.

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CHAPTER 71

Factors Affecting Incorporation of Bromide into Brominated Trihalomethanes During Chlorination

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Gary L. Amy, Paul A. Chadik, Zaid K. Chowdhury, Paul H. King, and William J. Cooper

Trihalomethanes (THMs) are formed during the chlorination of waters containing humic substances and other precursor compounds. Although chloroform is most often the predominant THM species, brominated haloforms can occur in waters containing bromide ion through the oxidation of bromide to hypobromous acid (HOBr) by hypochlorous acid (HOCl).[1] Thus, when waters containing bromide are chlorinated, chlorinated and brominated THMs are formed. An important concern in THM formation is the relative distribution of chloroform and brominated haloforms. Individual THM species vary in their amenability to removal by various treatment technologies as well as their suspected health hazards. Chloroform is the most volatile THM species and is removed effectively by air stripping, whereas bromoform is the species most effectively adsorbed by activated carbon.[2]

It is well known that bromide ion concentration affects both the rate of formation and the species distribution of THMs.[3,4] Although chlorine preferentially acts as an oxidant, bromine is more effective as a halogen-substituting agent.[5] Moreover, precursors from different sources may vary in their susceptibility toward either chlorination or bromination reactions. Stevens[6] noted that bromine substitution is favored over chlorine even when chlorine is present in large excess compared with the bromide concentration. If HOBr acts as an oxidant, it will be reduced to bromide ion, which may then be reoxidized by chlorine. These factors are responsible for the higher percentage of bromine vs chlorine incorporated into THM species.

Several researchers[3,4,6] have observed trends in species distribution as a function of initial bromide concentration when all other parameters are held constant. Bromoform increases while chloroform decreases as a nonlinear function of initial bromide. Bromodichloromethane increases with bromide to a maximum concentration of bromodichloromethane and thereafter decreases. Dibromochloromethane behaves in a similar manner except that the maximum concentration occurs at a higher initial bromide level. Based on work with humic acid, Stevens[6] found the total molar yield of trihalomethanes to increase with increasing bromide. A similar trend was noted by Oliver[4] in analyzing an

aquatic fulvic acid. Minear and Morrow,[7] in studying a natural water spiked with humic acid, also observed an increase in THM yield as bromide increased, both on a weight and a molar basis. They noted that the increase in THM formation caused by bromide appeared to level off at high bromide concentrations, ostensibly because of the limiting amount of nonvolatile total organic carbon (NVTOC) available for reaction.

A percentage of the ambient bromide present in a water is transformed and incorporated into THM species. Cooper et al.[8] suggested that some bromide not recovered in THMs may have become associated with higher-molecular-weight organobromine compounds or, in the presence of ammonia, may appear as bromamines.

Cooper et al.[8] studied bromide incorporation during the chlorination of a highly colored groundwater. For a reaction time of 144 h, the percentage of bromide incorporated into THM species increased as a function of bromide concentration to a maximum and thereafter decreased. Given the ambient bromide level of the water[9] and the incremental addition of further bromide, this maximum occurred at a Br^- concentration of approximately 330 μg/L. Luong et al.[10] studied the effects of spiking a diluted natural water with bromide. Based on bromide additions of 50, 500, and 2000 μg/L, the percentages of bromide incorporated into THMs were determined to be 15, 28, and 11%, respectively. Considering the low ambient level of bromide (<30 μg/L), a maximum occurred at about 500 μg/L. Minear and Morrow[7] studied the effects of adding bromide to a river water spiked with humic acid. Based on data derived from a 96-h reaction time, the percentage of the bromide incorporated into brominated haloforms increased through a maximum of 40% at very low bromide levels (approximately 50 to 60 μg/L) and then declined steadily with increasing bromide until reaching a minimum of 5% at a bromide concentration of 8 mg/L.

Variables that affect THM formation and speciation include temperature, pH, chlorine dose, bromide ion concentration, precursor source and concentration, and reaction time.[11] The same variables may also influence the extent of conversion of inorganic bromide to organically bound bromine incorporated into THMs (THM-Br). Our objective in this chapter is to define the effects of each of the variables mentioned on the formation of THM-Br and the related conversion of inorganic bromide to THM-Br, expressed as "percentage conversion" [(THM-Br/Initial Br^-) × 100]. It should be noted that bromine may be incorporated into organic compounds other than THMs; however, these other forms of organic bromine are not included in THM-Br as defined herein.

EXPERIMENTAL

To study bromide incorporation, nine natural waters were subjected to experimental evaluation: the Edisto River (South Carolina), the Scioto River (Ohio), the Verde River (Arizona), the Biscayne Aquifer (Florida), the Ilwaco Reservoir (Washington), the Kaw Reservoir (Oklahoma), the Grasse River (New York), the Pearl River (Mississippi), and the James River (South Dakota).

As indicated in Tables I and II, these waters embrace a broad range of raw water quality characteristics: nonvolatile total organic carbon (NVTOC), 3.0 to 13.8 mg/L; ambient pH, 6.1 to 8.3; ambient Br^-, 10 to 245 μg/L; UV absorbance (at 254 nm and pH 7), 0.063 to 0.489; and color, 5 to 93 color units. Each water was studied in a series of experiments encompassing the following parameters and ranges of conditions:

Temperature = 10, 20, 30°C

pH = ambient, ambient + 1.5 units, ambient −1.5 units (Waters were held constant at the respective pH values with 0.1 *M* buffers.)

Br^- = ambient, ambient + 0.25 mg/L, ambient + 0.50 mg/L, ambient + 1.0 mg/L

Cl_2/NVTOC = 0.5, 1.0, 3.0, 5.0

Reaction time = 0.1, 0.5, 1, 2, 4, 8, 24, 48, 96, 168 h

Kinetic experiments (i.e., THM formation as a function of reaction time) were run for various combinations of experimental conditions. A set of "baseline" conditions was defined as follows: 20°C, ambient pH, ambient Br^-, and Cl_2/NVTOC ratio of 3.0. This set of conditions constitutes a "baseline" experiment, which represents the first kinetic experiment run for each water. Next, a related set of experiments was run in which each parameter was varied separately while other parameters were held constant at baseline levels. Thus, considering the above parameter ranges, two additional experiments were run to evaluate the effects of temperature and pH, respectively. Similarly, three additional experiments were run to study the effects of chlorine-to-NVTOC ratio and bromide. Subsequently, two more experiments were conducted to bracket the effects of the specified parameters: a "high extreme" experiment involving parameter levels most conducive to THM formation (i.e., 30°C, ambient pH + 1.5 units, ambient Br^- + 1.0 mg/L, and Cl_2/NVTOC = 5) and a "low extreme" experiment based on parameter levels least conducive to THM formation (i.e., 10°C, ambient pH − 1.5 units, ambient bromide, and Cl_2/NVTOC = 0.5).

A Dohrman DC-80 Carbon Analyzer was used for NVTOC determinations and a Perkin-Elmer UV-Visible Spectrophotometer (Model 200) was used for UV absorbance measurements. Bromide analyses were accomplished by two methods: a spectrophotometric technique[12] applicable to levels ranging from 1 to 100 μg/L (with higher levels measured by dilution) and a single-column ion chromatograph (Dionex Model 10) having a lower practical detection limit of about 100 μg/L. Trihalomethane formation potential (THMFP) was measured by introducing a buffered sample (phosphate or borate buffer) into a headspace-free septa-sealed serum vial. Sodium hypochlorite was then introduced via syringe, the vial was placed in a constant-temperature module, and the THM reaction was allowed to proceed for a designated reaction time. The

Table I. Summary of Raw Water Characteristics

Water	NVTOC (mg/L)	UV Absorbance[a]	THMFP[b] µg/L	THMFP[b] µmol/L	Ambient pH
Edisto	11.3	0.489	1083	9.00	7.30
Scioto	6.25	0.152	336	2.73	7.56
Verde	3.00	0.063	97	0.75	8.31
Biscayne	6.50	0.251	296	2.33	7.31
Ilwaco	6.00	0.329	405	3.27	6.10
Kaw	5.22	0.153	267	2.01	7.72
Grasse	6.56	0.288	490	4.09	6.83
Pearl	5.62	0.136	303	2.49	6.55
James	13.8	0.296	694	5.56	8.00

[a]254 nm, pH 7.0.
[b]168 h, pH 7.0, 20°C, Cl_2/NVTOC = 3:1.

Table II. Summary of Bromide Analyses

Water	Ambient Bromide Concentration (µg/L) Spectrophotometric Method	Ion Chromatographic Method	Assumed Value[a]
Edisto	74	<100	74
Scioto	96	100	98
Verde	109	112	111
Biscayne	161	140	151
Ilwaco	129	100	115
Kaw	162	142	152
Grasse	10	[b]	10
Pearl	51	[b]	51
James	245		245

[a]Based on average or spectrophotometric method if level below sensitivity of IC method.
[b]Not detected.

reaction was terminated with excess thiosulfate, and the resultant THM species were measured using liquid/liquid extraction and a Hewlett Packard 5794 gas chromatograph equipped with an electron capture (EC) detector.

RESULTS AND DISCUSSION

Data for the various reaction times were examined to study the kinetics of inorganic bromide conversion and the corresponding formation of THM-Br. To determine the effects of various factors on the percentage incorporation of bromide, a series of linear regression analyses was performed using that portion of the data base that would isolate the effects of a given variable (i.e., data in which a given variable was varied while all other variables were held constant). Linear regressions were separately performed for both long-term data (arbitrarily defined as a reaction time of 96 h) and short-term data (arbitrarily defined as a reaction time of 1 h). These regressions evaluated percentage conversion vs either pH, temperature, applied chlorine concentration, or initial bromide concentration. Precursor-related parameters (NVTOC, UV absorbance) were also evaluated, but little correlation was observed.

Effects of Reaction Time

The formation of THM-Br as a function of reaction time for selected waters is shown in Figure 1. The data shown in this figure correspond to the baseline data previously discussed. For the waters shown, levels of THM-Br ranged from <10 to >50µg/L. These THM-Br formation curves mimic the general shape of THM formation curves in which an initial phase of rapid formation is followed by a subsequent phase of slower formation and, eventually, a leveling off as any reactant approaches depletion. The data in Figure 1 suggest that THM-Br levels off at different times for different water samples following an initial rapid phase formation and a subsequent slower phase of formation. We also observed that although THM-Br levels off at different times further chloroform formation continued for these same waters. This may be consistent with the results of other researchers showing that the formation kinetics for each THM species differ.[13]

An alternative representation of data appears in Figure 2, portraying percent of conversion as a function of reaction time. This approach normalizes the data shown in Figure 1. It is apparent that a positive nonlinear trend exists between percent of conversion and reaction time. Linearization of the data could be accomplished by data transformation in which percent of conversion was regressed against the log of reaction time.

From Figure 2 it appears that the slope of the curves, percent of conversion vs reaction time, is generally the same for all four waters. However, there does not appear to be a simple relationship between the percent of conversion and NVTOC, Br^-, or chlorine concentration. For example, it can be seen that two waters having significantly different bromide levels, the Kaw Reservoir and Grasse River, exhibit approximately the same percent of conversion. On the other hand, the water obtained from the Biscayne Aquifer and the Edisto River, although markedly different in Br^- and NVTOC, gave similar percentage conversion curves as a function of time. One variable not included in this analysis that could account for some of these variations is ammonia, because chloramines (and, to a lesser extent, bromamines) could reduce the THM-Br. The formation of monochloramine would inhibit the oxidation of Br^-, and the formation of bromamines might inhibit the incorporation of organically bound bromine in THMs.

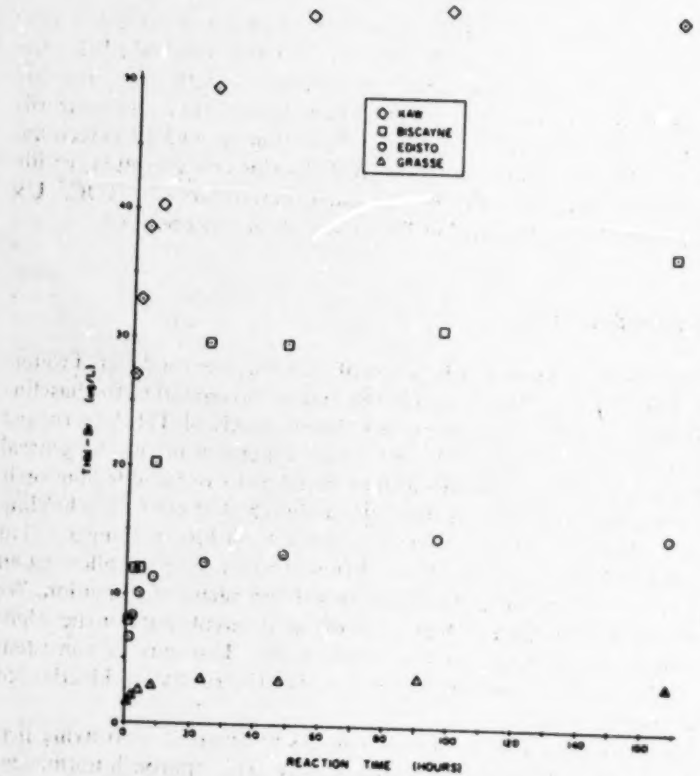

Figure 1. Formation of THM-Br as a function of reaction time for selected waters.

Effects of pH

In general, it was observed that TTHM yield (in micromoles per liter and in micrograms per liter) increased with increasing pH. All other variables being constant, a strong positive correlation was observed between percentage conversion and pH for each water. Linear regressions were performed for both long-term (96 h) and short-term (1 h) data for each water, using portions of the data base that isolate the effects of pH. Values of the coefficient of determination, r^2, based on long-term data were >0.9 for seven of the nine waters, whereas corresponding r^2 values for short-term data were >0.9 for five of the nine waters.

A graphical representative of percentage conversion vs pH is presented in Figure 3 for selected waters. Generally, slopes for long-term data were greater

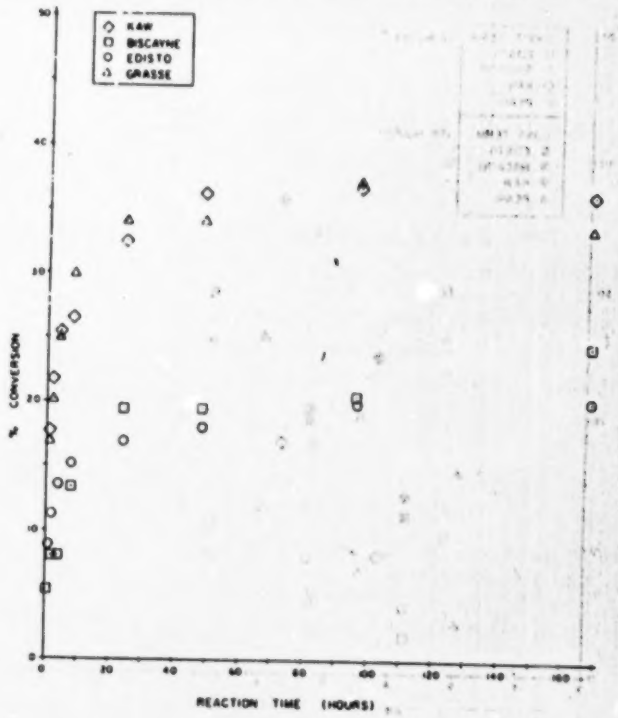

Figure 2. Percentage conversion as a function of reaction time for selected waters.

than corresponding slopes for short-term data, suggesting that differences between short-term and long-term bromide incorporation are greater at high pH levels. It is evident that the effect of pH on percentage conversion is a function of the nature of the particular water under evaluation. Based on the diversity in statistically derived estimates of slope and intercept, a universal response to pH is not exhibited by all waters. Incremental increases of about 2 to 7% per unit increase in pH were found for long-term reaction times, whereas for short-term reaction times, incremental increases ranged from 1 to 4%.

Effects of Temperature

An analysis of the data isolating the effects of temperature indicated that TTHM yield increased (on both molar and weight bases) as a function of

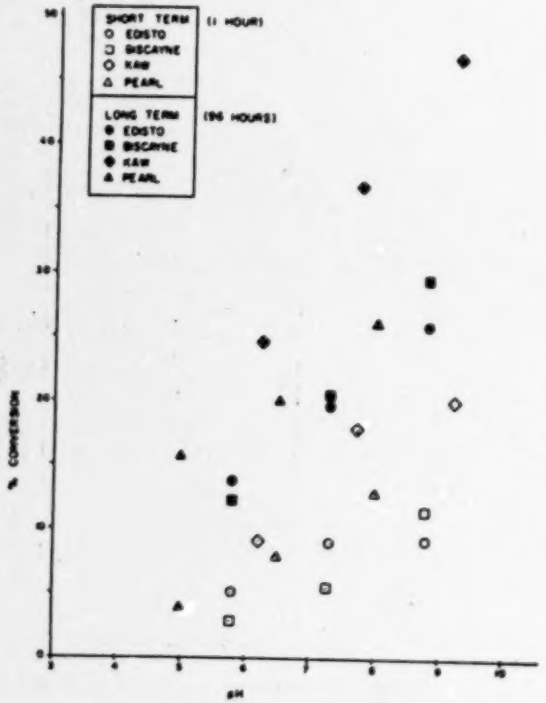

Figure 3. Percentage conversion as a function of pH for selected waters.

temperature. As with pH, a strong positive correlation was observed between percentage conversion and temperature in the range under consideration. A graphical representation of temperature effects is presented in Figure 4 for selected waters. As noted with respect to pH, each water responded uniquely to changes in temperature. Slopes associated with long-term data were generally steeper than corresponding slopes for short-term data, indicating more pronounced differences at higher temperatures.

It should be noted that in this evaluation of temperature (as well as subsequent evaluations of chlorine, bromide, and precursor) pH was held constant at the ambient level for a given water. Ambient pH levels for the various waters ranged from 6.1 to 8.3. Therefore, although most of the variation in response from water to water may result from changes in temperature (or another variable as discussed in subsequent discussions), some variation may also be attributed to differences in ambient pH.

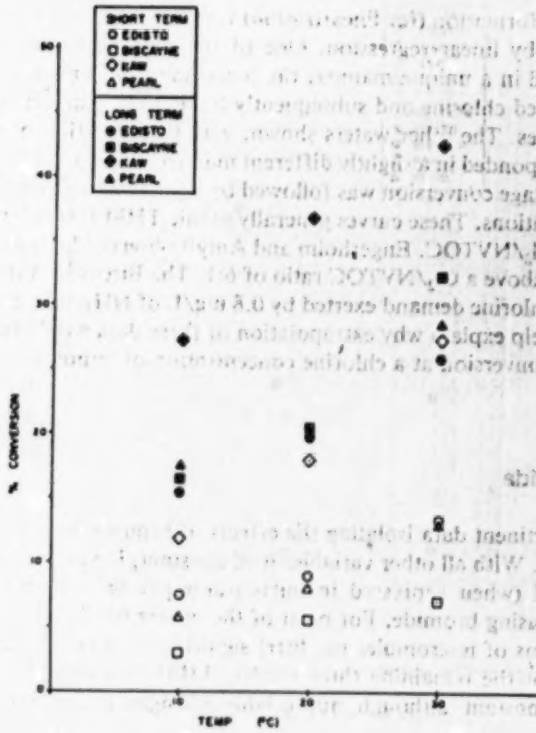

Figure 4. Percentage conversion as a function of temperature for selected waters.

Linear regression analysis of either long-term or short-term data gave values of r^2 that were greater than 0.9 for seven of the nine waters, indicating general linear trends. Considering statistically derived estimates of the slopes of regression equations, it can be expected that about a 0.5 to 0.9 % increase in percentage conversion will occur per degree centigrade increase for a reaction time of 96 h, whereas for the short-term reaction time, a corresponding increase of about 0.2 to 0.8 % can be expected.

Effects of Applied Chlorine Concentration

It was observed that TTHM increased as a function of applied chlorine. A positive, although nonlinear, correlation was observed between percentage conversion and applied chlorine. A graphical representative of the effects of chlorine on the incorporation of bromide appears in Figure 5 for selected

waters. Data transformation (for linearization) would be required before analyzing these data by linear regression. One of the waters shown, the Kaw Reservoir, behaved in a unique manner: the percentage conversion increased sharply with applied chlorine and subsequently leveled off, both at long and short reaction times. The other waters shown, with the exception of the Biscayne Aquifer, responded in a slightly different manner in that the initial rapid increase in percentage conversion was followed by a gradual increase at higher chlorine concentrations. These curves generally mimic THM formation curves as a function of Cl_2/NVTOC. Engerholm and Amy[14] observed little additional THM formation above a Cl_2/NVTOC ratio of 6:1. The Biscayne Aquifer was found to have a chlorine demand exerted by 0.8 mg/L of NH_3-N, a characteristic that would help explain why extrapolation of these data would indicate a zero percentage conversion at a chlorine concentration of approximately 6 to 7 mg/L Cl_2.

Effects of Bromide

Analysis of pertinent data isolating the effects of bromide revealed several interesting trends. With all other variables held constant, it was found that, in all cases, TTHM (when expressed in micrograms per liter) increased as a function of increasing bromide. For most of the waters (six of nine), TTHM (expressed in terms of micromoles per liter) significantly increased with bromide, whereas for the remaining three waters, THM molar yields remained approximately constant although appreciable changes in speciation were observed.

The percentage conversion trends as a function of bromide for all waters varied. As bromide levels increased in the range of the experimental matrix, percentage conversion decreased for five waters, increased for two waters, and increased through a maximum before decreasing for two waters. Trends for both short- and long-term data were similar. Previously run experiments using larger bromide concentration ranges helped explain this phenomenon. The results of these experiments (168-h reaction time) are portrayed in Figure 6, which shows percentage conversion as a function of bromide level for three selected waters. For the Biscayne Aquifer, the decreasing percentage conversion is demonstrated throughout the bromide range. For the Verde River, an increase is shown up to a bromide level of 0.361 mg/L and then a decrease is shown at higher bromide levels. The Scioto River curve is similar to that of the Verde, but the maximum is located at a higher bromide level. Similar trends of increasing followed by decreasing percentage conversion as a function of bromide ion concentration were observed for other waters, but the bromide level for maximum percentage conversion was different in all cases. For two of the waters, the apparent maximum occurred at a bromide concentration of greater than the highest level studied during the kinetic experiments (ambient + 1.0 mg/L). This explains why analysis of the long-term and short-term data indicated a positive correlation between percentage conversion and bromide for these particular waters.

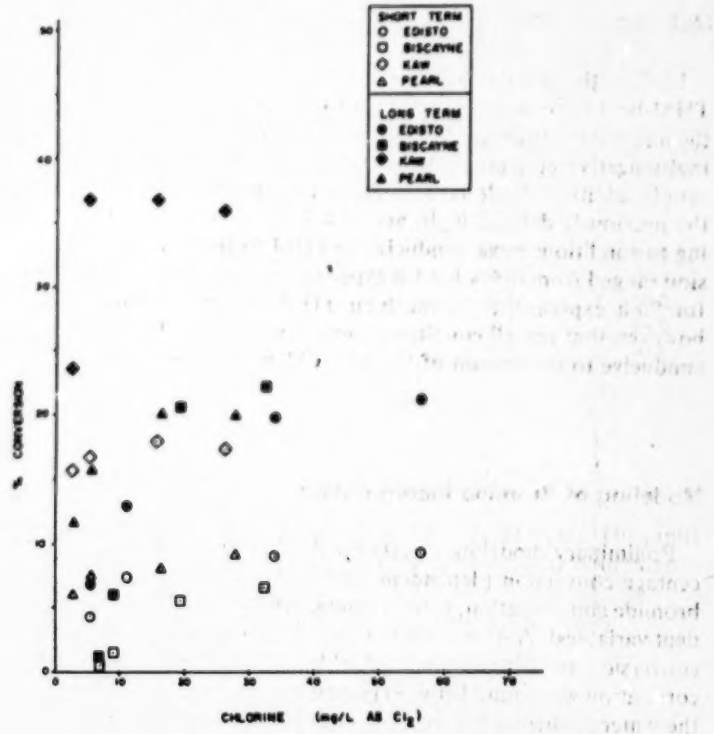

Figure 5. Percentage conversion as a function of chlorine concentration for selected waters.

Effects of Precursor Source

Based on the previous discussion, it is apparent that each water exhibited a unique response to changes in experimental variables, which suggests that the precursor source and concentration affect bromide incorporation. However, simple linear regressions between percentage conversion and two precursor-related parameters, NVTOC and UV absorbance, yielded r^2 of <0.1 when either short-term or long-term data associated with the baseline experiment were analyzed. This finding suggests that precursor effects are more complex than indicated by the above analysis. The role of precursor may be related to multiplicative effects with other factors such as ammonia, pH, and temperature.

Multiplicative Effects

Each of the previously discussed effects on percentage conversion of Br^- to THM-Br were based on portions of the data base that isolated the effects of the particular variable being analyzed. It is expected that there are also various multiplicative effects involving two or more of these variables that are not simply additive. Table III summarizes the percentage conversion observed in the previously defined high- and low-THM extreme experiments corresponding to conditions most conducive to THM formation. The percentage conversion ranged from 0.5% for 1-h experiments in the low THM extreme to 64.6% for 96-h experiments in the high THM extreme. It should be recognized, however, that not all conditions most conducive to THM formation are most conducive to conversion of Br^- to THM-Br (i.e., Br^- concentration).

Modeling of Bromide Incorporation

Preliminary modeling efforts involved a series of regressions between percentage conversion (dependent variable) vs temperature, pH, chlorine dose, bromide concentration, reaction time, NVTOC, and UV absorbance (independent variables). A strong positive correlation was observed between percentage conversion and temperature, pH, chlorine dose, and reaction time. An inverse correlation was found between percentage conversion and bromide for most of the waters, whereas a very poor correlation was noted for both NVTOC and UV absorbance. Plots of percentage conversion vs each of the independent variables (x) indicated some departures from linearity. In many cases, data transformation ($\ln x$, x^2, $\sqrt{x}$, $1/x$) improved linearity and facilitated the use of multiple linear regression techniques in formulating a model.

A computerized multiple linear regression program[15] was used to analyze the data. A series of stepwise multiple linear regressions was performed to evaluate various forms and combinations of variables. Separate regressions were conducted for each water in addition to an overall regression of data for all waters. Not all of the data base was used for these regressions. Data derived from experiments involving incremental bromide additions, as well as data associated with the high and low extreme experiments, were not included because of the complexity of modeling the nonlinear effects of bromide. All other data were used (nine waters, four Cl_2/NVTOC ratios, three pH levels, three temperatures, and ten reaction times).

The regressions involved percentage conversion vs arithmetic as well as transformed values of each independent variable. Based on analysis of partial correlation coefficients, the stepwise multiple linear regression technique, when analyzing all data, entered the following variables into the equation during the first five steps in the indicated sequence; (1) ln (reaction time),

Table III. Percentage Conversion Observed in Low- and High-THM Extreme Experiments

Water	Short-Term (1 h)		Long-Term (96 h)	
	Low-THM Extreme	High-THM Extreme	Low-THM Extreme	High-THM Extreme
Edisto	2.8	23.5	10.1	52.4
Scioto	3.4	20.7	10.7	52.5
Kaw	5.5	18.1	16.5	64.3
Ilwaco	0.7	15.0	2.5	34.1
Pearl	1.3	23.9	6.3	50.3
James	0.5	26.5	3.7	64.6
Grasse	2.7	22.3	15.1	51.8

(2) (temperature)^2, (3) (1/bromide), (4) (pH)^2, and (5) (1/chlorine). The multiple coefficient of determination (R^2) was 0.66 for the following equation:

$$\text{percentage conversion} = -1.73 + 2.50 \ln(\text{reaction time}) + 0.0118(\text{temperature})^2 + 0.104(1/\text{bromide}) + 0.129(\text{pH})^2 - 17.1(1/\text{chlorine})$$

It can be seen that the regression coefficient for the chlorine-related term, inverse chlorine, is negative. This, of course, implies that chlorine concentration will have a positive effect on percentage conversion. This particular form of the chlorine variable was selected before other forms by the stepwise regression techniques, based on a comparison of partial correlation coefficients for the variables remaining after the previous step. Also, during the stepwise analysis, a precursor-related parameter was not entered into the equation until the eighth step, in which $(NVTOC)^2$ was entered; however, this entry into the equation provided an incremental change in R^2 of only 0.005 over the previous step. This suggests that the relationship between bromide incorporation and precursor is more complex than the above type of analysis assumes.

Next, the same stepwise technique was applied to data for each of the waters individually. Bromide-related variables were not considered, because the bromide level was constant for each water. In most, but not all cases, the same variables in the previous equation (except for 1/bromide) were entered into the equations before other transformed variables although the sequence of entered variables differed somewhat for each of the waters. Multiple R^2 values after four steps were >0.84 for seven of the waters and >0.90 for five of the waters. Finally, as an alternative analysis to the stepwise approach, data for

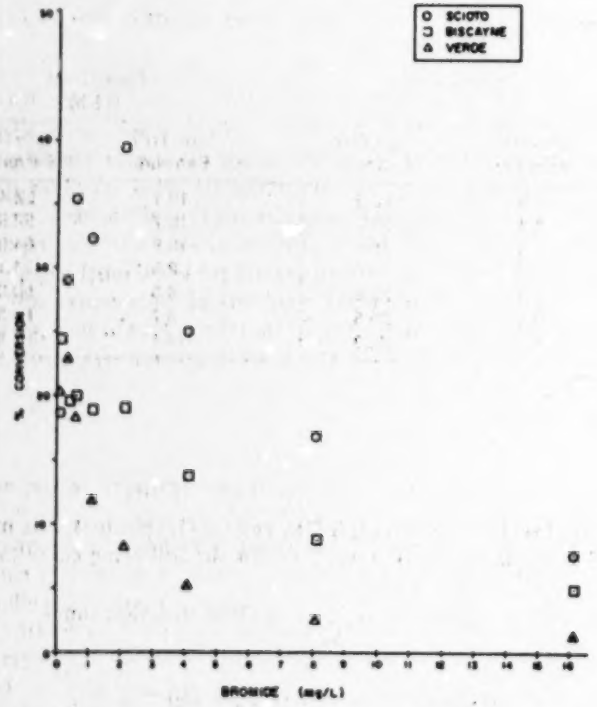

Figure 6. Percentage conversion as a function of bromide concentration for selected waters (168-h reaction time).

each water were regressed against the specific variables determined for the general model shown above (except 1/bromide). Multiple R^2 values were >0.82 for seven of the waters and >0.92 for four of the waters. The higher R^2 values observed for the individual water regressions compared to the overall regression suggests that, although the various waters respond in a somewhat similar manner to the variables, the magnitude of the responses varies from water to water.

CONCLUSIONS

In THM formation a portion of the inorganic bromide ion concentration is converted to organically bound bromine in the three common brominated THM species. This percentage conversion (1) increases rapidly in the first stages of THM formation and approaches a plateau at longer reaction times; (2) increases with increasing pH and increasing temperature; (3) increases with chlorine concentration but approaches a plateau at high concentrations; (4) initially increases with Br^- concentration to a maximum percentage conversion and subsequently decreases at higher Br^- concentrations.

It was difficult to define clear trends for the variation of percentage conversion with THM precursor source and concentration presumably because of multiplicative effects of variables as well as parameters such as ammonia concentration that were not examined in this study.

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